LA-UR- 01-4490

Approved for public release; distribution is unlimited.

Title: QUANTUM MOLECULAR DYNAMICS AND EOS

Author(s): Joel D. Kress

Submitted to: LANL Energetic Materials Review 2001. Los Alamos, NM, Aug. 6 - 9, 2001.

Los Alamos
NATIONAL LABORATORY

Quantum Molecular Dynamics and EOS

Joel D. Kress
Theoretical Division
Los Alamos National Laboratory

LANL Energetic Materials Review
August 6-9, 2001

OUTLINE

- Introduction to quantum molecular dynamics
- Principal hugoniots for shock-compressed Deuterium, Nitrogen and Oxygen
- Pressure-dependent frequency shifts for dense Nitrogen and mixtures of dense Nitrogen/Carbon monoxide
- Status Report on MondoSCF: New Methods for the Ab Initio Simulation of Large Systems

Quantum Molecular Dynamics (QMD)

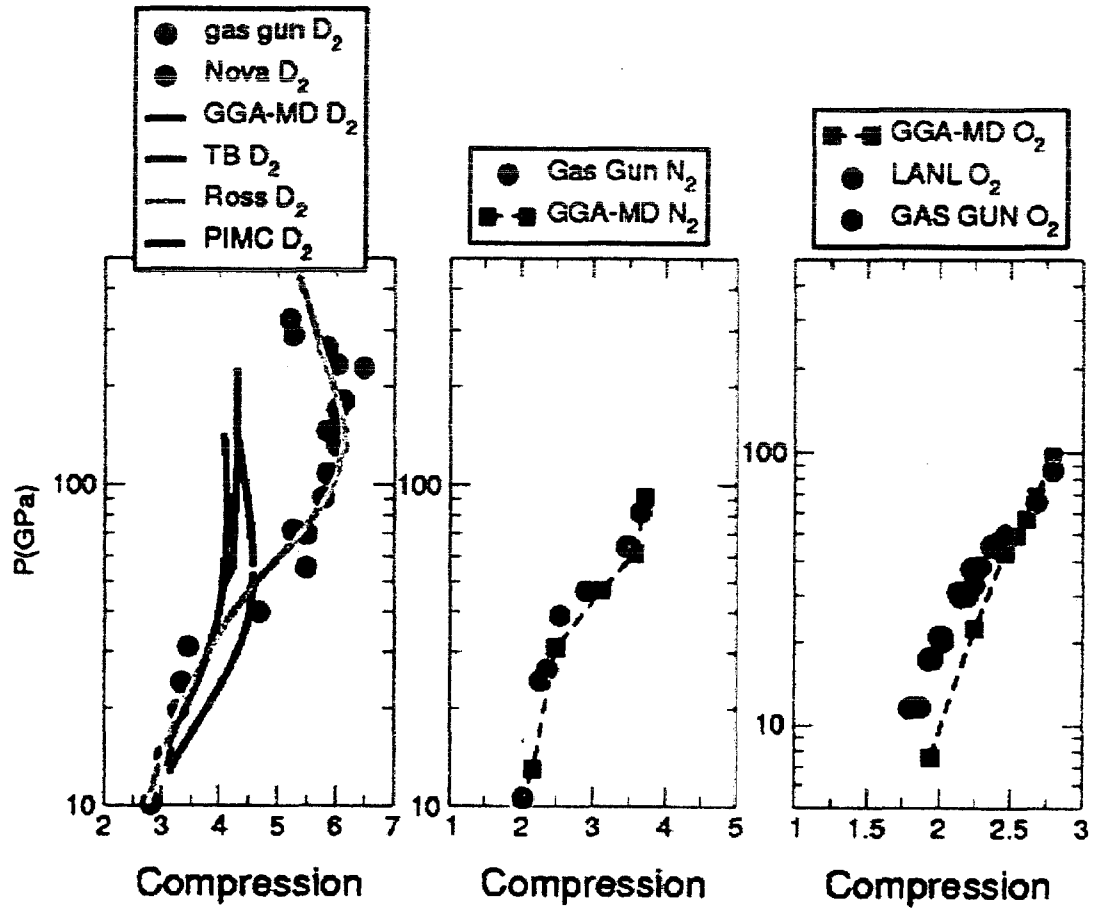
- System: 3-D periodic cell of N atoms and valence electrons
- Electrons: quantum mechanical treatment ($H\Psi=E\Psi$)
  - Interatomic potential derived from electronic wavefunctions
  - Accurate description of bond breaking and bond making
- Nuclei: classical treatment ($F=ma$)
- MD trajectory: alternate repeatedly between steps 2 and 3

Density Functional Molecular Dynamics Simulations of Shocked Molecular Fluids

J. D. Kress, S. Mazevet, L. A. Collins,
J. D. Johnson, W. W. Wood
Theoretical Division, Los Alamos National Laboratory
P. Blottiau
CEA, Bruyeres Le Chatel, France

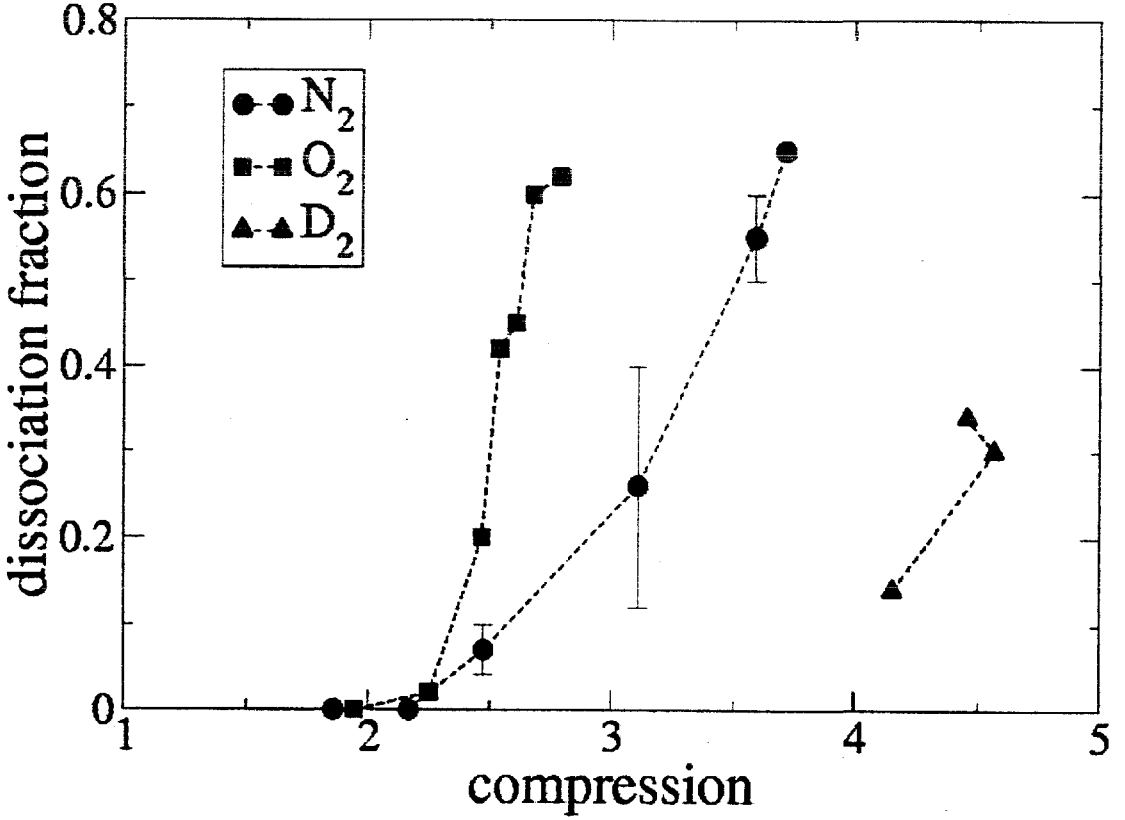
LANL Energetic Materials Review
August 6-9, 2001

Hugoniots for Deuterium, Nitrogen and Oxygen: Exp't vs. ab initio Molecular Dynamics (GGA-MD)



Los Alamos

Inflection Point in P-ρ Space Along Hugoniot Correlates with the Onset of Molecular Dissociation



Theoretical EOS for Detonation Products
A Monte Carlo/Perturbation Theory Approach

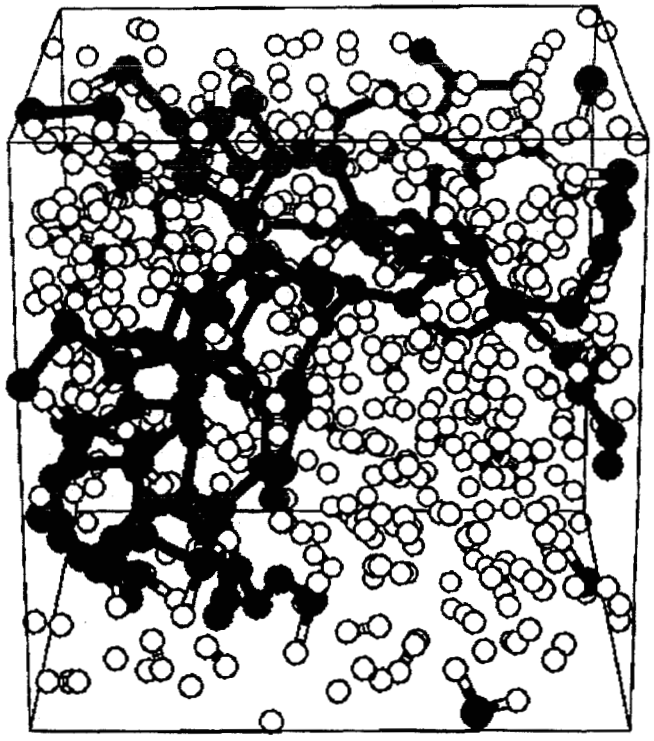
Detonation products include CO_2, N_2, H_2O, and solid carbon

Carbon clusters modeled with dangling bonds on surface capped with various radicals composed of C, H, N, and O from the fluid

Presently - additive model used to estimate the cluster-radical bond strength

Proposal - use ab initio calculations for surface-radical bond strengths

Simulation of C:H mixture (1:4 ratio) at T=6000 K and P=50 GPa. (Note the carbon cluster network.)

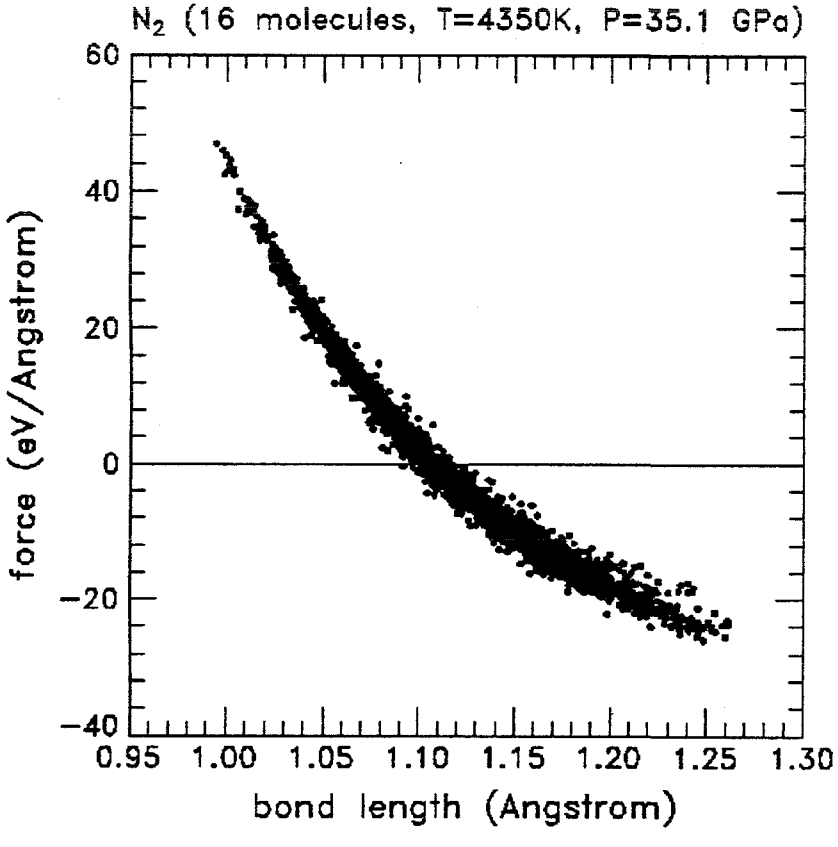


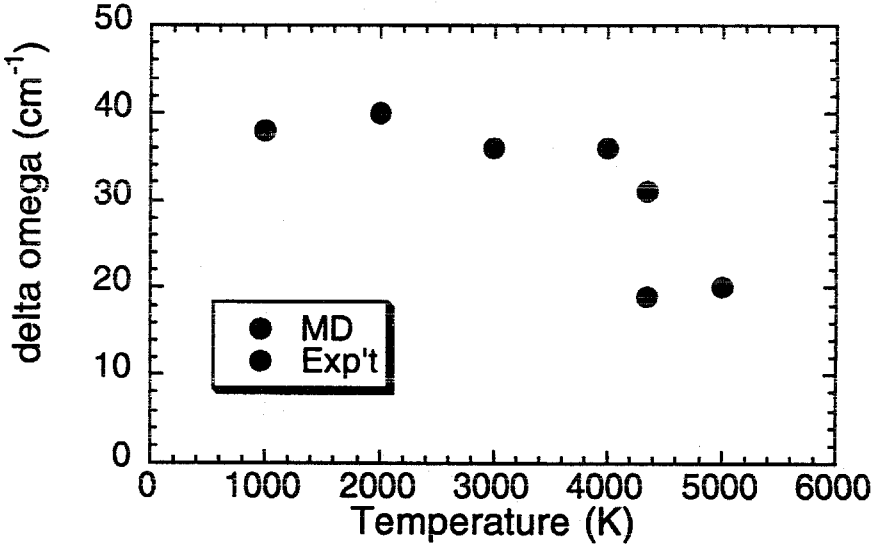
N_2 Gas-phase Results

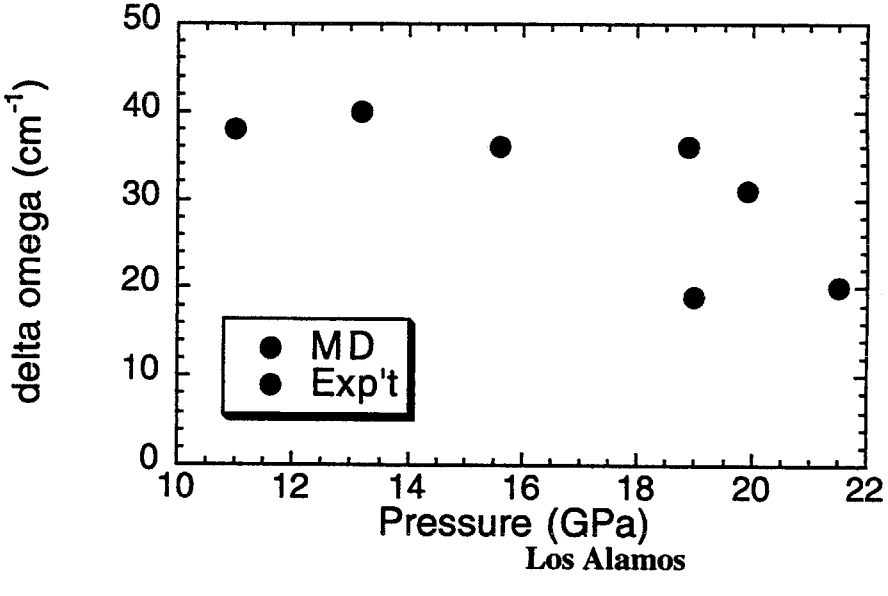
Method	Basis	R_e (Å)	ω (cm^{-1})	
G98/PW91	6-31+G*	1.1151	2362	
G98/B3LYP	6-31+G*	1.1051	2454	
VASP/PW91	435 eV	~1.14	1566	(MD period)
VASP/PW91	435 eV	1.1148	1611	(MD forces)
VASP/PW91	517 eV	1.1131	1623	(MD forces)
Exp't		1.098	2359	

Pressure-Dependent Frequency Shifts Extracted from Density Functional Molecular Dynamics (VASP-MD)

- Quartic polynomial fit to bond forces averaged over fixed temperature MD







Pressure-Dependent Frequency Shifts Extracted from ab initio Molecular Dynamics (VASP-MD)

- Comparison to CARS exp'ts. of Moore et al. (1988) for shock-compressed nitrogen

- $\Delta\omega$(exp't) = measured 0->1 Raman shift

  $\Delta\omega$(MD) = frequency shift (shifts relative to uncompressed fluid)

		P (GPa)	P (GPa)	$\Delta\omega$ (cm^{-1})	$\Delta\omega$ (cm^{-1})
ρ(g/cc)	T(K)	exp't	MD	exp't	MD
2.14	4350	35	35	38	25
1.75	4340	19	20	19	31
1.78	2400	16	17	28	33

MondoSCF: New Methods for the Ab Initio Simulation of Large Systems

M. Challacombe and C . J. Tymczak
Theoretical Division
Los Alamos National Laboratory

LANL Energetic Materials Review
August 6-9, 2001

Electronic Structure Codes
3D Periodic Boundary Conditions

MondoSCF (Challacombe, Tymczak et al.)

- Density functional theory (BLYP)
- Gaussian basis functions
- N-scaling (CPU work scales linearly with no. of atoms)

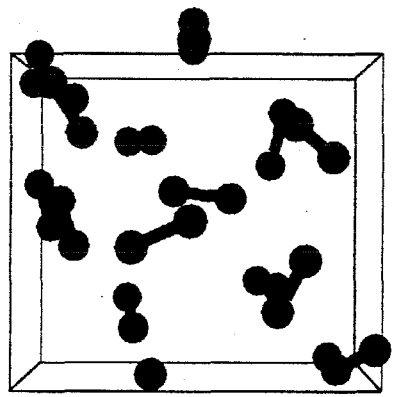
VASP (Vienna ab initio Simulation Package)

- Density functional theory (GGA/PW91)
- Planewave basis functions
- Ultrasoft pseudopotentials for core electrons
- N^2-scaling

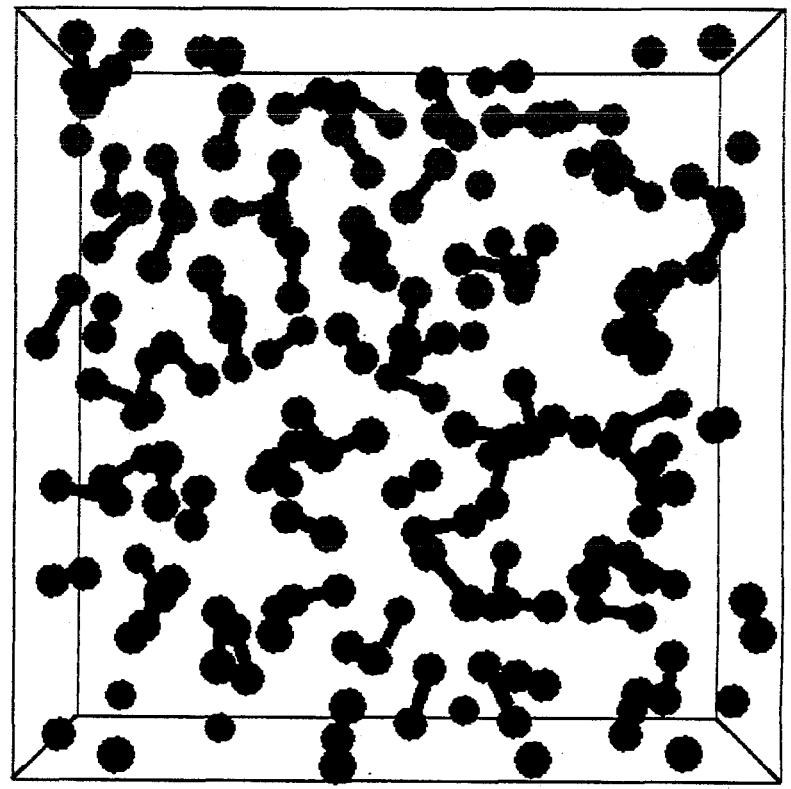
Dense Nitrogen (ρ = 2.1 g/cc, T=3090 K)

Density-Functional (VASP) Molecular Dynamics (MD)
Snapshots of 3D-Periodic Simulation Cell

32 atoms, L = 7.1 Å
160 valence electrons



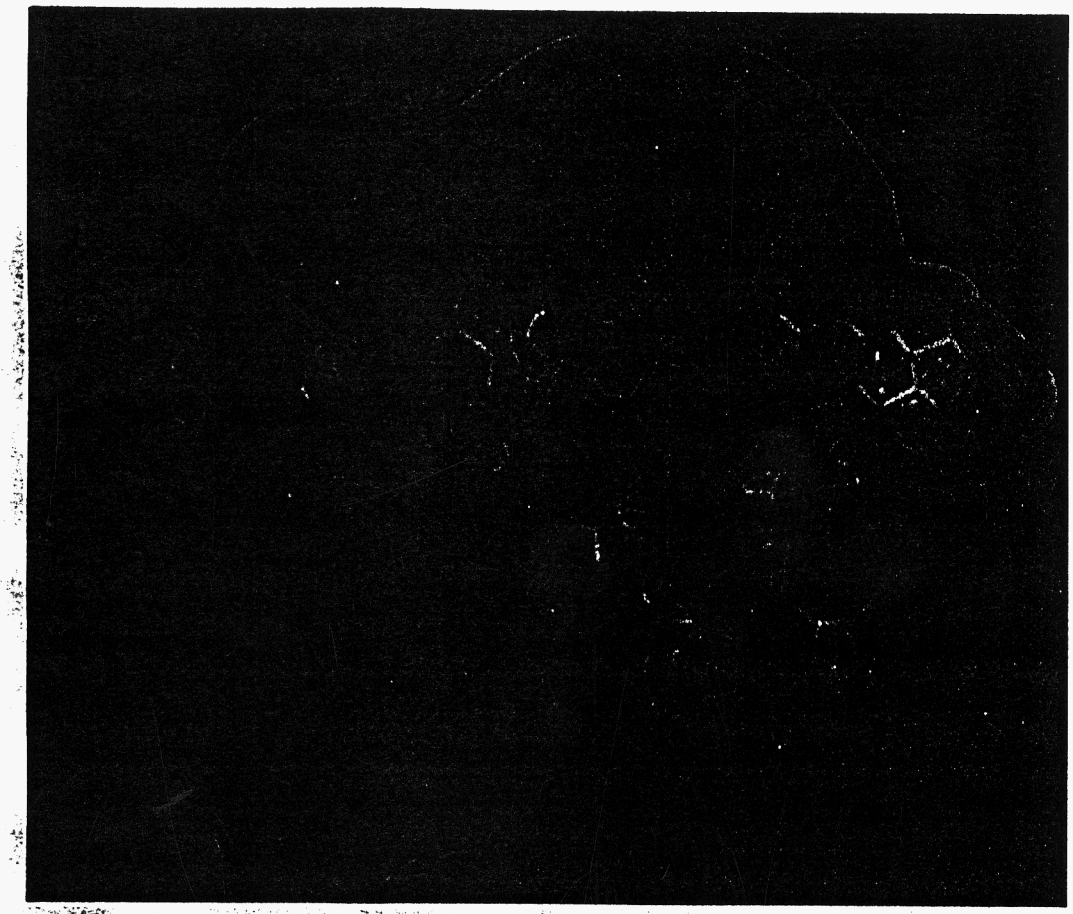
202 atoms, L = 13.1 Å
1010 valence electrons



Los Alamos

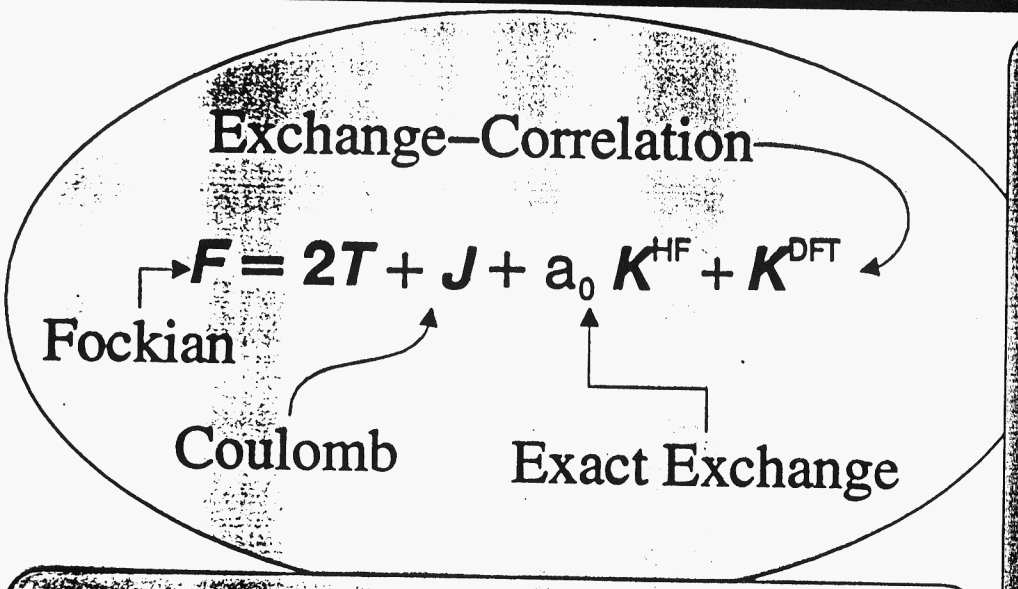
New Methods for the *Ab Initio* Simulation of Large Systems

Matt Challacombe and Mike Salazar
Theoretical Division, Group T-12
Los Alamos National Laboratory



- *O*(*N*) SCF theory and the **MondoSCF** project
- Hierarchical methods for Coulomb and Exchange–Correlation matrices
- Analytic gradients and geometry optimization
- Parallel atom–blocked sparse matrix algebra for *O*(*N*) SCF theory

MondoSCF[#]: A Suite of Programs for $O(N)$ SCF Theory



- Hybrid Hartree Fock/Density Functionals such as B3LYP achieve chemical accuracy (2 kcal/mol)
- The potential exists for the very large scale (10,000 atom) application of HF/DFT using parallel $O(N)$ methods

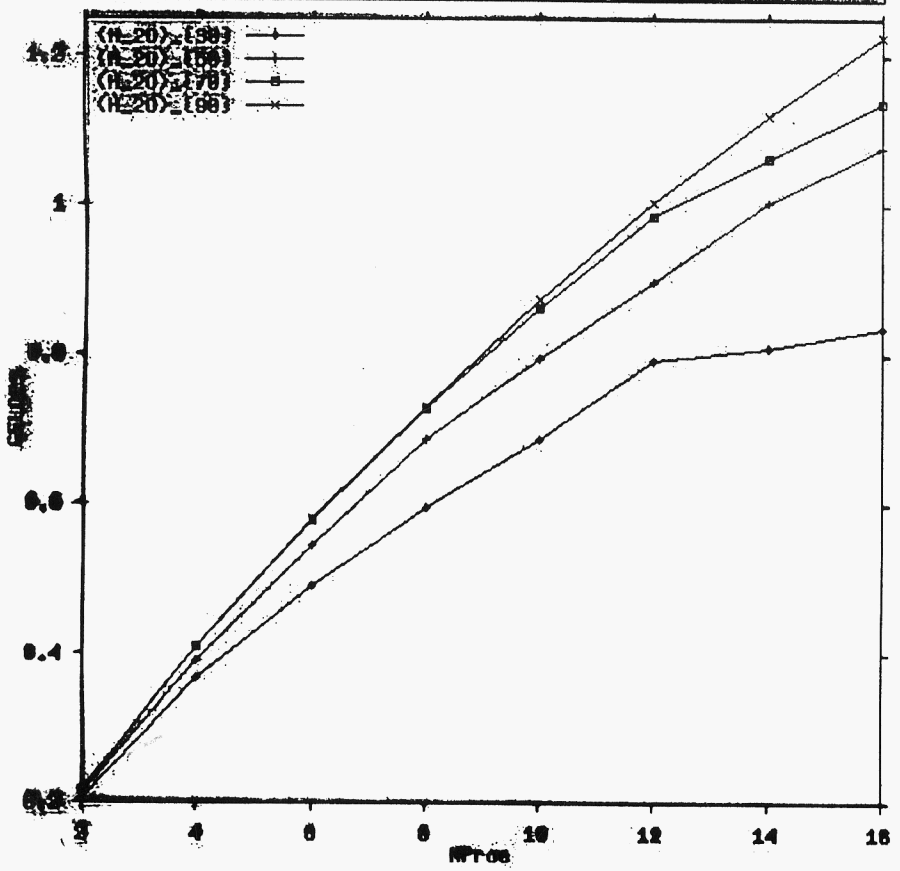
- Equivalence with standard LCAO Quantum Chemistry
- OO F95, MPI and HDF5
- In the public domain
- Target capabilities
  - ✓ Full linear scaling for LCAO HF/DFT
  - ✓ Periodic boundaries
  - ✓ Analytic gradients
  - ✓ Massive parallelism

[#]mondo [SoCal] *adj. slang* As an intensifier: considerable, much, huge.

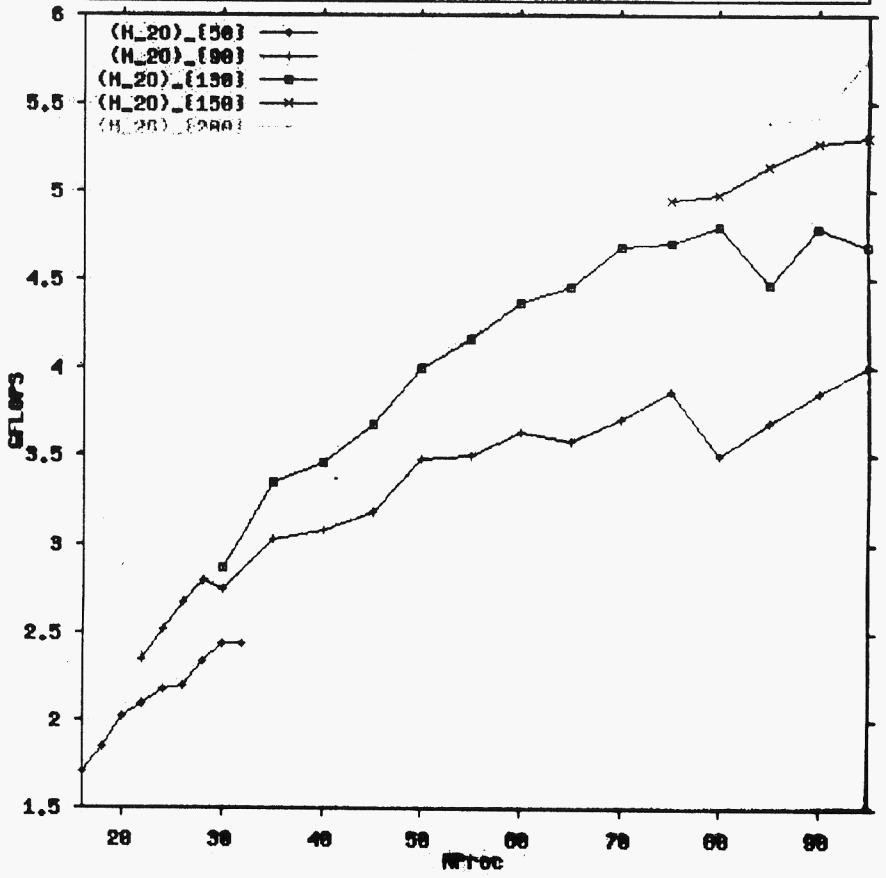
Sustained Performance of || Sparse–Blocked Linear Algebra for SDMM

- Performance determined by granularity
- Running out of memory for large BlueMtn calcs (256MB/Node)
- Lots of room for improvement!

300Mhz PII/Myrinet



BlueMountain (180Mhz R10K)



Summary

- Proof of principle: $O(N)$ achieved in all target areas except orthogonalization (very cheap $O(N^2)$, work in progress to get linear).

- Parallel methods are essential to enable large routine calculations because of sizable memory and cost prefactors.

- **Parallel** sparse matrix infrastructure has been developed supporting **future work on parallel QCTC, HiCu and ONX and corresponding gradients.**

Acknowledgments

- C.J. Tymczak (Periodic Boundary Conditions; T–14, LANL)
- Eric Schwegler (ONX; LLNL)
- M. Salazar (Forces; T–12, LANL)
- US Department of Energy under contract W–7405–ENG–36, Los Alamos ASCI high explosives project